THE EFFECT OF SULPHURIC ACID ON THE DEPOSITION OF METALS WHEN USING A MERCURY CATHODE AND ROTATING ANODE.

By LILY G. KOLLOCK and EDGAR F. SMITH.

[Contribution from the John Harrison Laboratory of Chemistry.]

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In the course of a study of the precipitation of metals with the help of a mercury cathode and rotating anode, observations were made which led to a review of the experiments to ascertain more especially what effect varying amounts of acid would have upon the electrolytic decomposition of certain metallic sulphates.

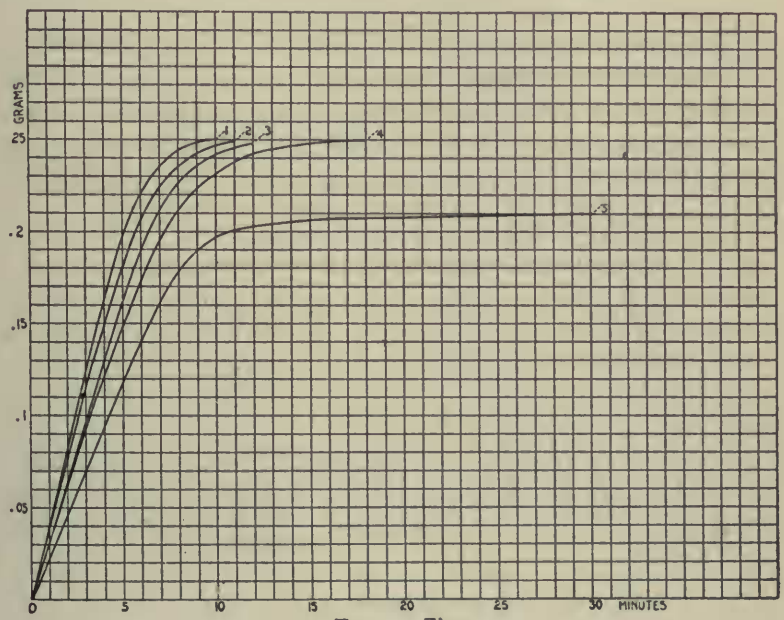

Fig. 1. Zinc.

The metals studied under these conditions were zinc, copper, cadmium, iron, cobalt and nickel. The volume of the solution of the salt was, in nearly all cases, ten cubic centimeters, containing

about 0.25 gram of metal. The current was maintained at two amperes, while the pressure varied from 4 to 4.5 volts. The sulphuric acid was concentrated. Curves were plotted from the results obtained.

Zinc.

When one cubic centimeter of sulphuric acid was present in a solution of zinc sulphate, the zinc was completely deposited in ten minutes. The solution contained 0.25 gram of metal, the volume of the solution being eleven cubic centimeters. The following observations were made:

In 2.5	minutes,	0.1040	gram	of zinc	was deposited.
" 5	"	0.1974	"	"	"
" 7.5	"	0.2400	"	"	"
" 8	"	0.2428	"	"	"
" 10	"	0.2494	"	"	"

(Figure 1, Curve 1.)

When two cubic centimeters of sulphuric acid were present, the solution, which was siphoned from the cup, showed the presence of a trace of zinc after it had been electrolyzed for ten minutes. Eleven minutes were necessary for the complete removal of the zinc. The volume of the solution in this case was twelve cubic centimeters. The following rate of deposition was observed:

In 2.5	minutes,	0.0953	gram	of zinc	was deposited.
" 5	"	0.1805	"	"	"
" 7.5	"	0.2306	"	"	"
" 10	"	0.2467	"	"	"
" 11	"	0.2488	"	"	"

(Figure 1, Curve 2.)

In the presence of three cubic centimeters of acid, twelve minutes were required for the deposition of the zinc. The volume of the solution in these experiments was thirteen cubic centimeters. Under these conditions—

In 2.5	minutes,	0.0815	gram	of zinc	was deposited.
" 5	"	0.1633	"	"	"
" 7.5	"	0.2200	"	"	"
" 10	"	0.2428	"	"	"
" 12	"	0.2493	"	"	"

(Figure 1, Curve 3.)

When four cubic centimeters of acid were present, considerable retardation in the decomposition was observed; for at the end of the fifteen minute period, there was still some undeposited zinc. The test at the end of eighteen minutes showed that no zinc was present in the solution. The rate of precipitation was as follows:

In 2.5	minutes,	0.0668	gram of	zinc	was deposited.
" 5	"	0.1506	"	"	"
" 7.5	"	0.2050	"	"	"
" 10	"	0.2315	"	"	"
" 12	"	0.2423	"	"	"
" 15	"	0.2480	"	"	"
" 18	"	0.2495	"	"	"

(Figure 1, Curve 4.)

That the presence of five cubic centimeters of acid greatly retards the precipitation was shown when a solution, containing 0.2110 gram of zinc, was electrolyzed. It was thirty minutes before the last traces of metal were thrown out.

In 2.5	minutes,	0.0668	gram of	zinc	was deposited.
" 5	"	0.1306	"	"	"
" 10	"	0.1980	"	"	"
" 20	"	0.2077	"	"	"
" 30	"	0.2110	"	"	"

(Figure 1, Curve 5.)

In these experiments the volume of the solution was increased, in each case, by the addition of the acid. Thinking that, perhaps, the increased period of time might be due to the greater volume of solution, it was observed that the retardation was due principally to the acid present. From a solution of fourteen cubic centimeters volume, containing one cubic centimeter of sulphuric acid, all the zinc was deposited in twelve minutes. In the same volume of solution, containing four cubic centimeters of acid, eighteen minutes were necessary for complete precipitation.

Copper.

The volume of the copper sulphate solution in these experiments, as well as in the solutions of the sulphates of the succeeding metals, was ten cubic centimeters, including the volume of the acid added.

The amount of copper present in the solution was 0.2485 gram.

In the presence of one cubic centimeter of sulphuric acid, all the copper was deposited in ten minutes. The current registered two amperes and showed a pressure of from 3 to 3.5 volts. The solution became colorless in seven minutes. Three minutes additional were

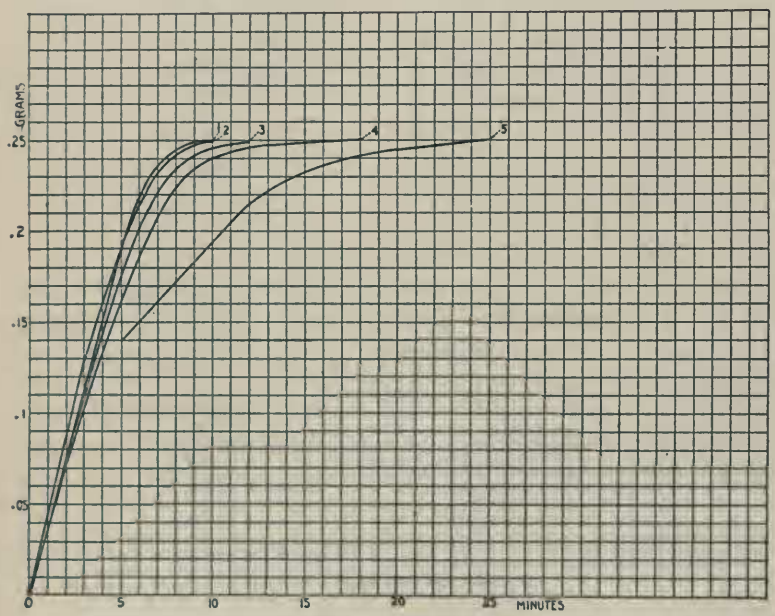

FIG. 2. Copper.

necessary to deposit the remaining 0.007 gram of copper. The following rate of precipitation was observed:

In 2.5	minutes,	0.0985	gram of	copper	was deposited.
" 5	"	0.1887	"	"	"
" 7.5	"	0.2418	"	"	"
" 10	"	0.2437	"	"	"

(Figure 2, Curve 1.)

When two cubic centimeters of acid were present and the current was maintained at two amperes, the pressure varying from 4 to 4.5 volts, it was found that the copper was completely deposited in ten minutes. It will be observed that the pressure in this case was half a volt to a volt greater than in the previous experiment. The two curves almost coincide.

In 2.5	minutes,	0.1157	gram	of copper	was deposited.
" 5	"	0.1897	"	"	"
" 7.5	"	0.2385	"	"	"
" 10	"	0.2489	"	"	"

(Figure 2, Curve 2.)

The presence of three cubic centimeters of acid affects the curve but slightly. The departure is noticed in the deposition of the last traces of the metal. The copper was completely removed in twelve minutes.

In 2.5	minutes,	0.1079	gram	of copper	was deposited.
" 5	"	0.1807	"	"	"
" 7.5	"	0.2311	"	"	"
" 10	"	0.2450	"	"	"
" 12	"	0.2488	"	"	"

(Figure 2, Curve 3.)

The effect of a large amount of sulphuric acid was noticed again in the latter part of the decomposition, when four cubic centimeters of acid were added. It was then observed that it took six minutes longer than it did when but three cubic centimeters were present to remove all copper.

In 2.5	minutes,	0.1060	gram	of copper	was deposited.
" 5	"	0.1684	"	"	"
" 7.5	"	0.2078	"	"	"
" 10	"	0.2402	"	"	"
" 12	"	0.2458	"	"	"
" 18	"	0.2487	"	"	"

(Figure 2, Curve 4)

In the presence of five cubic centimeters of acid, twenty-five minutes were necessary in order that the last traces of copper might be removed. The solution did not become colorless until after eighteen minutes.

In 5	minutes,	0.1422	gram	of copper	was deposited.
" 10	"	0.1943	"	"	"
" 12	"	0.2140	"	"	"
" 15	"	0.2334	"	"	"
" 20	"	0.2451	"	"	"
" 23	"	0.2476	"	"	"
" 25	"	0.2484	"	"	"

(Figure 2, Curve 5.)

From a neutral solution of the salt, under the same conditions, the copper was completely precipitated in eight minutes.

Cadmium.

In the presence of one cubic centimeter of sulphuric acid, 0.25 gram of cadmium was deposited in ten minutes. The current equaled two amperes, and the pressure from 4 to 4.5 volts.

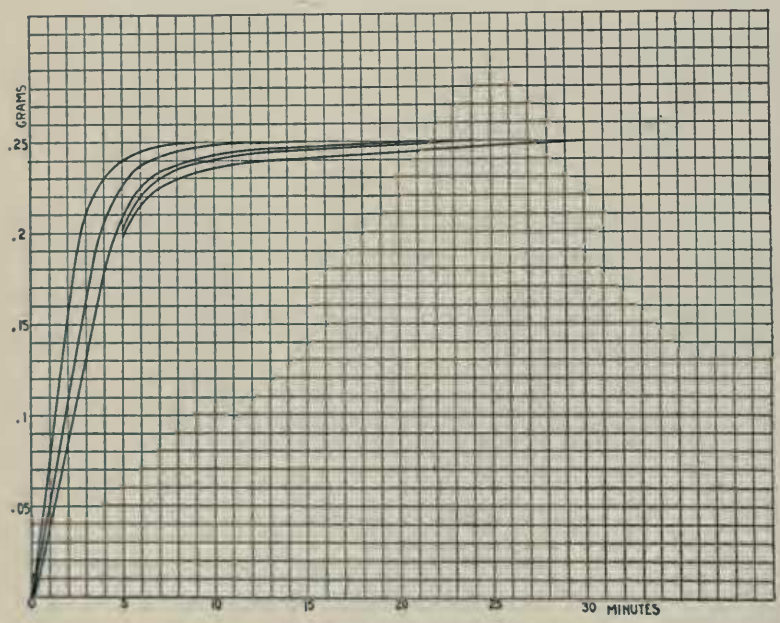

Fig. 3. Cadmium.

In 2.5	minutes,	0.1720	gram of	cadmium	was deposited.
" 5	"	0.2418	"	"	"
" 7.5	"	0.2480	"	"	"
" 10	"	0.2500	"	"	"

(Figure 3, Curve 1.)

When two cubic centimeters of acid were present, hydrogen sulphide, after fifteen minutes, gave a faint yellow color to the solution from the cell. In eighteen minutes there was no color on testing the liquid in the same way.

In 2.5	minutes,	0.1250	gram of	cadmium	was deposited.
" 5	"	0.2260	"	"	"
" 7.5	"	0.2398	"	"	"
" 10	"	0.2439	"	"	"
" 15	"	0.2480	"	"	"
" 18	"	0.2501	"	"	"

(Figure 3, Curve 2.)

Twenty-two minutes were required to precipitate all of the cadmium in the presence of three cubic centimeters of acid.

In 5	minutes,	0.2028	gram of	cadmium	was deposited.
" 7.5	"	0.2260	"	"	"
" 10	"	0.2433	"	"	"
" 15	"	0.2475	"	"	"
" 20	"	0.2486	"	"	"
" 22	"	0.2498	"	"	"

(Figure 3, Curve 3.)

When four cubic centimeters of acid were added to the electrolyte, twenty-seven minutes were necessary for the complete precipitation of the cadmium.

In 5	minutes,	0.2023	gram of	cadmium	was deposited.
" 10	"	0.2392	"	"	"
" 15	"	0.2491	"	"	"
" 20	"	0.2488	"	"	"
" 25	"	0.2495	"	"	"
" 27	"	0.2505	"	"	"

(Figure 3, Curve 3.)

When five cubic centimeters of acid were present in the solution, at the end of thirty-five minutes there was considerable cadmium undeposited (.003).

In 5	minutes,	0.1974	gram of	cadmium	was deposited.
" 10	"	0.2354	"	"	"
" 20	"	0.2419	"	"	"
" 30	"	0.2454	"	"	"
" 35	"	0.2475	"	"	"

(Figure 3, Curve 5.)

Iron.

Sulphuric acid retards the decomposition of iron sulphate to a far greater extent. Even after forty minutes, in the presence of one cubic centimeter of acid, a trace of iron was held in solution.

In 5 minutes, 0.0858 gram of iron was deposited.
" 10 " 0.1204 " " "
" 15 " 0.1639 " " "
" 20 " 0.2196 " " "
" 30 " 0.2439 " " "
" 35 " 0.2481 " " "

(Figure 4.)

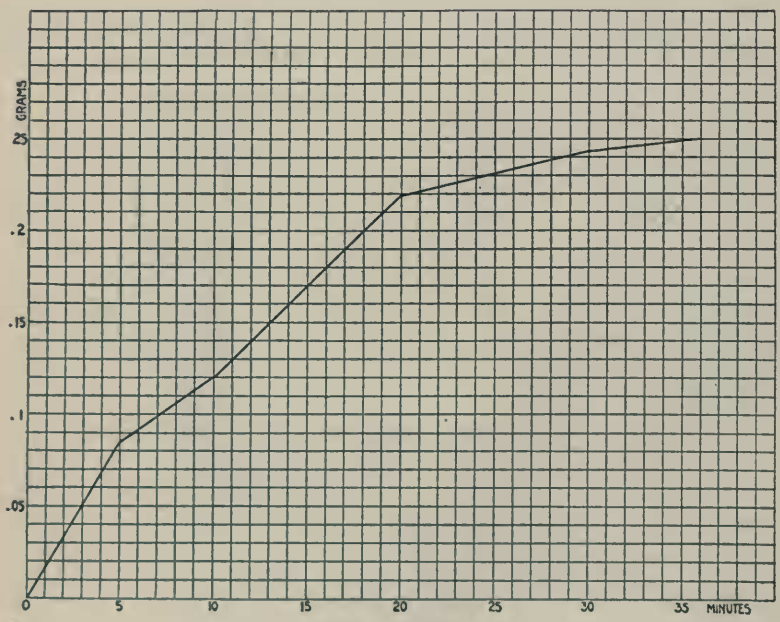

FIG. 4. Iron.

In the presence of three cubic centimeters of acid, in twenty-five minutes, .069 gram of iron was found in the mercury. Four cubic centimeters of acid were not enough to completely hold up the iron.

NICKEL.

In fifteen minutes the nickel solution, containing one cubic centimeter of sulphuric acid, became colorless. It required twenty minutes, however, to remove the last traces of metal.

In 5 minutes, 0.1404 gram of nickel was deposited.
" 10 " 0.2070 " " "
" 15 " 0.2370 " " "
" 20 " 0.2476 " " "
" 25 " 0.2511 " " "

(Figure 5, Curve 1.)

In the presence of two cubic centimeters of acid, after twenty minutes, the solution gave a brown color after adding ammonium hydroxide and ammonium sulphide. In thirty minutes the test showed that there was still a small amount of nickel unprecipitated.

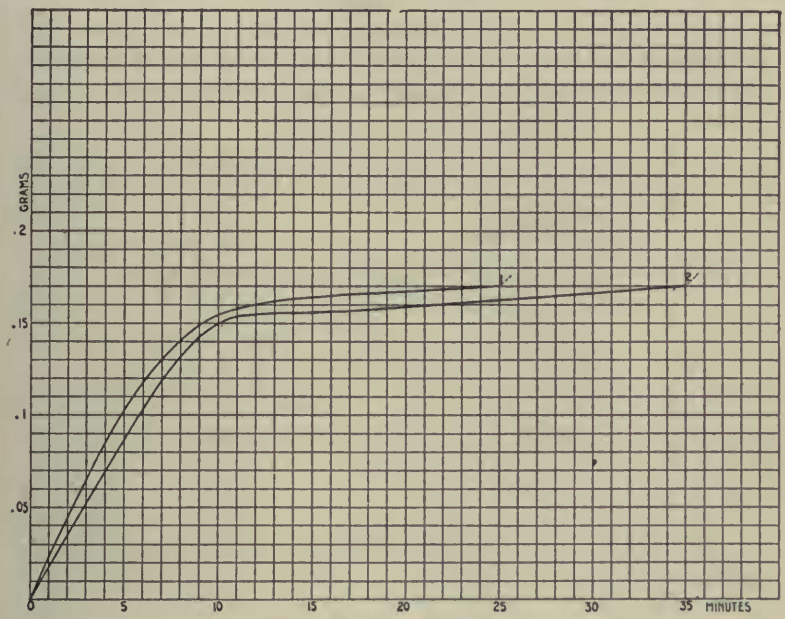

FIG. 5. Nickel.

In thirty-two minutes nickel was found in the solution siphoned from the cup.

In 5	minutes,	0.1265	gram of	nickel was	deposited.
" 10	"	0.2053	"	"	"
" 15	"	0.2290	"	"	"
" 20	"	0.2383	"	"	"
" 25	"	0.2445	"	"	"
" 30	"	0.2485	"	"	"
" 32	"	0.2500	"	"	"

(Figure 5, Curve 2.)

COBALT.

The solution of cobalt sulphate contained 0.1700 gram of cobalt. Twenty-five minutes were required for its complete precipitation in the presence of one cubic centimeter of sulphuric acid.

In 5	minutes,	0.1010	gram	of cobalt	was deposited.
" 10	"	0.1539	"	"	"
" 15	"	0.1663	"	"	"
" 20	"	0.1681	"	"	"
" 25	"	0.1700	"	"	"

(Figure 6, Curve 1.)

When two cubic centimeters of sulphuric acid were present, ten minutes additional were necessary for the removal of the cobalt.

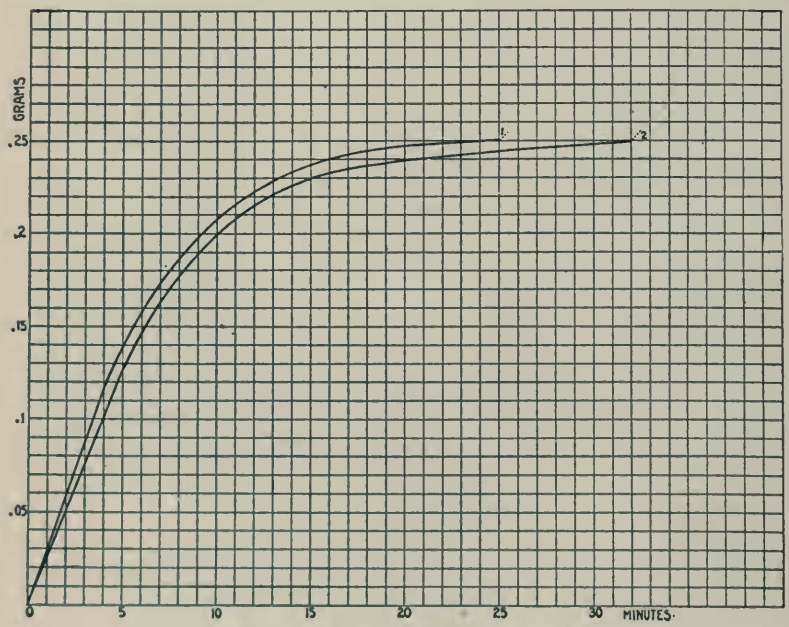

FIG. 6. Cobalt.

In 5	minutes,	0.0859	gram	of cobalt	was deposited.
" 10	"	0.1496	"	"	"
" 15	"	0.1555	"	"	"
" 25	"	0.1669	"	"	"
" 35	"	0.1709	"	"	"

(Figure 6, Curve 2.)

The ease and rapidity with which metals are precipitated upon the mercury cathode naturally suggested the inquiry as to the separations which were possible in this manner. The following lines

communicate a few results obtained in this direction. The idea will, however, be pursued in detail as far as it can be carried out.

Cadmium from Aluminium.

The aluminium salt appears to retard the complete deposition of cadmium. In the presence of a few (4) drops of concentrated sulphuric acid with a current of two amperes and seven volts, considerable cadmium remained undeposited after the current had acted fifteen minutes. A higher current was, therefore, employed. The separation was complete in twenty minutes, using a current of three amperes and seven volts. The cadmium in solution was 0.25 gram, while the aluminium sulphate was equivalent to 0.1 gram of aluminium. The total volume of the solution was ten cubic centimeters. The increase in the weight of the mercury in the first experiment was 0.2502 gram and in the second 0.2495 gram.

Cadmium from Magnesium.

This separation was accomplished under the same conditions as the previous separation (cadmium from aluminium).

Conditions.

Volume of solution	= 10 cubic centimeters.
Magnesium sulphate	= 0.1 gram magnesium.
Cadmium sulphate	= 0.25 gram cadmium.
Sulphuric acid	= 4 drops (40 drops = 1cc.).
Current	= 2–3 amperes.
Pressure	= 11–9 volts.
Time	= 25 minutes.
Cadmium found (first experiment)	= *0.2505 gram.*
Cadmium found (second experiment)	= *0.2497 gram.*

Cadmium from Chromium.

Inasmuch as chromium is deposited from its sulphate from slightly acidulated solution, the separation of chromium from cadmium was carried out in the presence of three cubic centimeters of concentrated acid. The conditions were as follows:

Volume	= 10 cubic centimeters.
Chromium sulphate	= 0.1 gram chromium.
Cadmium sulphate	= 0.25 gram cadmium.
Sulphuric acid	= 3 cubic centimeters.

Current	= 2–3 amperes.
Pressure	= 3.5–4 volts.
Time	= 25 minutes.
Cadmium found (first experiment)	= *0.2499 gram.*
Cadmium found (second experiment)	= *0.2492 gram.*

Copper from Aluminium.

This separation was accomplished in the presence of 0.5 cubic centimeters of sulphuric acid (1.1). The current registered 1 ampere and 4 volts. In four minutes the solution was colorless. The current was allowed to act for ten minutes.

Volume of the solution	= 10 cubic centimeters.
Copper sulphate	= 0.1150 gram copper.
Aluminium sulphate	= 0.1 gram aluminium.
Sulphuric acid (1.1)	= 0.5 cubic centimeter.
Current	= 1–1.6 ampere.
Pressure	= 4–4.5 volts.
Time	= 10 minutes.
Copper found	= *0.1150* gram, *0.1153* gram, *0.1152* gram.

A low current (0.01 ampere and 2 volts) was passed through zinc sulphate in the presence of 0.25 cubic centimeter of sulphuric acid. In twenty minutes the mercury had increased 0.0006 gram in weight.

Iron sulphate containing 0.1110 gram of iron, acidulated with 0.5 cubic centimeter of acid, with a current of 0.01 ampere and a pressure of 2 volts gave in thirty minutes 0.0434 gram of iron. When one cubic centimeter of acid was present, a current of 0.1 ampere with a pressure of 2 volts gave 0.0991 gram of metal.

The separation of copper from zinc was attempted but it was not successful. A copper solution containing 0.1150 gram of copper, in the presence of 2.5 cubic centimeters of acid and a current of 0.6 ampere and three volts, caused the mercury to increase in weight 0.1360 gram, showing that 0.0212 gram of zinc had also been deposited.

The separation of copper from iron was tried, but this, too, failed. With a current (like that given in the preceding paragraph) iron was detected in the mercury, and in thirty minutes the solution still showed the presence of copper. 0.25 cubic centimeter of acid was present. The iron seemed to hold back the copper.

When three cubic centimeters of acid were present in a solution of iron sulphate, containing 0.1 gram of iron and it was electrolyzed with a current of two amperes and four volts, 0.069 gram of iron went into the mercury. The experiment was repeated after the addition of four cubic centimeters of acid. Even this quantity failed to hold up all the iron. The separation, therefore, of iron from copper and of iron from zinc was unsuccessful.

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